

Final Technical Report

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Center Name: Southern California Particle Center and Supersite (SCPCS)

Center Director: John R. Froines

Title: Particle Size Distributions of Polycyclic Aromatic Hydrocarbons in the LAB

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Project Period: June 1, 1999–May 31, 2005 (no-cost extension to May 31, 2006)

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RFA: Airborne Particulate Matter (PM) Centers (1999)

Research Category: Particulate Matter

Topic C: Studies of the Effects of Varying Spatial and Temporal Patterns of Ambient Particulate Matter (PM) and Co-pollutants and Resulting Health Effects with Emphasis on the Role of Atmospheric Chemistry

Objective(s) of the Research Project: While epidemiological studies have firmly established that fine particles (F) can adversely affect the health of exposed individuals, even at exposure levels at or below the current ambient air standard, several questions regarding F toxicity remain elusive, including:

1. Which chemical component(s) or class of components of F are the most hazardous?
2. In addition to atmospheric concentration, what other properties of F are important?
3. What role does particle size play in F toxicity?
4. How is the toxicity of F affected as it mixes and reacts with gaseous air pollutants and free-radicals during advective atmospheric transport?

Beginning with the work of Ferin (1992), firmly establishing the existence of dramatic differences in pathogenicity resulting from different particle sizes of the same material, laboratory and field studies reported over the last decade firmly demonstrated that the size of atmospheric particles determines: (1) the number of particles deposited at a tissue target, (2) where the particles deposit in the human respiratory system, (3) which aerodynamic mechanism governs their deposition in the respiratory tract, and (4) their atmospheric reactivity and life-times.

Particle size, concentration, and chemical composition are the aerosol properties that are among those likely to be most important to both chronic and acute toxicity. If we want understand, for regulatory purposes, how toxin-containing airborne particles are transported and transformed, we need to acquire detailed information of their particle size, concentration, and chemical

composition, during all seasons of the year, both near their emission sources and in locations where humans are exposed to the airborne aerosol.

The major objective of this research project, complementing other activities described elsewhere in the final reports of the Southern California Particle Center and Supersite (SCPCS), was to acquire information on the effects of season and location on the concentration, and the size distribution of polycyclic aromatic hydrocarbons (PAHs) (defined by the U.S. Environmental Protection Agency [EPA] as Priority Pollutants) collected in Southern California communities. Detailed size resolution in the ultrafine (UF) and Aitken (diameter $<50\text{ }\mu\text{m}$) size ranges constituted the ultimate foci of these studies.

Summary of Findings:

Achievement of Project's Objectives

We developed gas chromatography/mass spectrometry (GC/MS) and high-performance liquid chromatography (HPLC)-selective fluorescence methods to measure all 16 U.S. EPA Priority Pollutant PAHs present in source and ambient air samples (Pereira, et al., 2001; 2002; Eiguren-Fernandez, et al., 2003). Using the National Institute of Standards and Technology (NIST) standard reference material (SRM) 1649a, which contains certified concentrations for several PAHs, our extraction and quantification procedures provided overall analytical precision of 4.2% and extraction recovery efficiencies ranging from 92 to 97% for all PAHs. We also participated in the development and validation of a GC-MS derivatization-based method used to quantify quinones in diesel exhaust particles, and ambient $\text{PM}_{2.5}$ samples collected in the LAB and other Southern California locations (Cho, et al., 2004).

We went on to evaluate the extent of sampling artifacts that might occur during the collection of size resolved semi-volatile and particle-phase PAHs using MOUDI impactors with and without an annular denuder (Eiguren-Fernandez, et al., 2003).

Between 2001 and 2003, we measured the seasonal and spatial variation of F and vapor-phase PAH concentrations at all 12 communities participating in a multi-year chronic respiratory health study of schoolchildren in the Children's Health Study (CHS). The communities were geographically distributed over two hundred kilometers, extending from coastal Central California through coastal Los Angeles, inland to Riverside and San Bernardino counties, and south into Eastern San Diego County (Eiguren-Fernandez, et al., 2004; Miguel, et al., 2004).

Concurrently with the development and validation of accurate and sensitive methods for PAH quantification, we measured, during all seasons, the particle size distributions of 12 priority pollutant PAHs, concurrently with elemental carbon (EC), organic carbon (OC), sulfate (SO_4^{2-}), and nitrate (NO_3^-) size distributions. Samples were collected from October 2001 to July 2002 in Claremont, CA, a receptor site located about 40 km downwind of Central Los Angeles.

Our most recent observations of the size distributions of twelve target PAHs in the $10\text{ nm} < \text{Dp} < 2.5\text{ }\mu\text{m}$ size range, showed that, overall, regardless of vapor pressure, the PAH masses in

each of the differential fractions (10–18nm, 18–32nm, and 32–56nm) are larger in the smallest fraction (10–18 nm) than that in the two larger fractions (Miguel, et al., 2005).

Given our results that naphthalene (identified by the U.S. EPA as a hazardous air pollutant, and listed in the 2002 State of California's Proposition 65 program as a substance known to cause cancer) constitutes about 95% of the measured PAH mass, together with several SCPCS researchers, we carried out new field measurements of the naphthalene-to-benzene ratio at the busy Sepulveda Tunnel (under LAX) in Los Angeles, to support an advanced modeling study to quantify population exposure to the emissions of naphthalene throughout Southern California (Lu, et al., 2005).

The studies related to the toxicity of PAHs and quinones, and their concentration in diesel exhaust particles (DEP) used in *in vitro* experiments (Li, et al., 2000; 2004; Cho, et al., 2005) are reported in detail elsewhere in the final reports of the SCPCS.

Project's Significant Technical Details

Analytical and Sampling Methods Development. The use of annular denuders was recommended in the literature as a means of reducing "sampling artifacts." The hypothesis was that, by removing vapor-phase species before particle-phase collection, and then capturing any of the same vapor-phase species that remained after particle-phase collection, the effects of sampling artifacts could be corrected by comparing the levels of the species found associated with the particle-phase and that captured downstream. Our results showed that at a source and a receptor area in the LAB, using either sampling system, the size distributions obtained were similar for PAHs found in the particle-phase, but different for the semi-volatiles. At a central Los Angeles site, the largest PAH fraction was found in the UF size range, typical of primary emissions. At the downwind location, the largest fraction was in the accumulation size range, consistent with an "aged" aerosol. We concluded that sampling with the regular MOUDI configuration, i.e., without the use of an annular denuder, is simpler and thus recommended for measurement of the size distribution of PAHs in either group.

Seasonal and Spatial Variations of Vapor- and Particle-Phase PAH Levels. For all communities, we found that naphthalene (NAP) accounted for 95% of the total PAH mass, with annual averages ranging from 89 to 142 ng/m³. The highest values for benzo[ghi]perylene (BGP), a tracer of light-duty engine exhaust (present almost exclusively in the particle-phase), and of the pro-carcinogen benzo[a]pyrene (BAP) were observed in Long Beach and Lancaster. Annual averages of the pro-carcinogen BAP were also highest in Long Beach and Lancaster (Eiguren-Fernandez, et al., 2004; Eiguren-Fernandez, et al., 2007). A considerable increase in the particle-phase PAH level, relative to the vapor-phase, was observed as ambient temperature decreased. Cold/hot season ratios for PAHs in PM_{2.5} reached 54 at Long Beach. These data underscore the importance of seasonal variation on PAH concentration, expressed as lower surface and boundary inversion layers and reduced advective atmospheric mixing during the cold season, as compared with the effects of PAH chemical reaction with atmospheric gases and free-radicals during the hot season.

Seasonal Variation of the Size Distribution of PAH, EC and Major Ionic Species Downwind of Central Los Angeles. Samples were collected approximately once every week, for 24-hour periods, from midnight to midnight. MOUDI impactors samples were composited for analysis into monthly periods in three aerodynamic diameter size intervals, defined for the purpose of this report as ultrafine (UF), fine (F), and coarse (C). For the monthly composites from October to February, the size distributions of the target PAHs are similar. However, from March to July, notable differences were observed: a significant fraction of the PAH mass was found in the C, as compared with the previous period. During the entire 1-year period, the form and shape of the EC size distributions did not vary much and were distinguished by prominent mass in the UF and accumulation size mode. For the individual modes of the major species, the highest Pearson's correlation coefficients (r) for the variation of temperature with species concentration were found in the UF for both SO_4^{2-} (0.92) and EC (0.90), and in the C for both OC (0.85) and NO_3^- (0.54). High SO_4^{2-} correlations are consistent with increased gas-to-particle formation during the warmer months from (precursor) SO_2 emissions in the Los Angeles and Long Beach seaport areas and, similarly for EC, increased atmospheric transport to Claremont as the season progressed from winter to summer.

Observations of PAHs in the Aitken Size Range. Several dynamometer studies reported over the last decade, and more recently, from vehicle-chase studies (David Kittelson's group in Minnesota), showed that aerosols produced by spark-ignition and diesel engines and by other high-temperature processes contain nanoparticles in the Aitken, nucleation, accumulation mode, and often, fractal-like particles or agglomerates. Fuel and combustion generated PAHs that accumulate in the engine's lube oil are normally emitted through the exhaust system. Aitken size range PAHs may result from rapid cooling (self-nucleation) while the hot vapors move along the exhaust pipe into ambient air, or, as hypothesized by McMurtry (2004, personal communication) they may partition from the vapor-phase into oily droplets originated from self-nucleated lube oil. While it is still unknown at present, which mechanism(s) contribute to the observed mass in the Aitken size range, our most recent observations of the size distributions of the twelve target PAHs in the $10 \text{ nm} < \text{Dp} < 2.5 \text{ }\mu\text{m}$ size range, show that, for all target PAHs, regardless of vapor pressure, the masses in each of the differential fractions (10–18nm, 18–32nm, and 32–56nm) are larger in the smallest fraction than that in the two larger fractions (Miguel, et al., 2005). We found that, the masses in the UF size bin ranged from 100% for benzo[k]fluoranthene, benzo[a]pyrene, and indeno[1,2,3-cd]pyrene to 46% for anthracene, of the masses collected in the Aitken size range.

Modeling Study to Quantify Population Exposure to the Emissions of Naphthalene Throughout Southern California. Our results (Lu, et al., 2005) showed that gasoline and diesel engine exhaust, with related vaporization from fuels, were found to contribute roughly half of the daily total naphthalene burden in Southern California. A more detailed account of this study is reported elsewhere in the final reports of the SCPCS.

Results

Caldecott Tunnel Sampling Campaign. As part of Year 6 of our PM Center activities, we measured $\text{PM}_{2.5}$ emission factors, separately for heavy-duty diesel (HDD) and light-duty vehicles (LDV), of volatile, semi-volatile and particle-phase ($\text{PM}_{2.5}$) PAHs, over summer (2004) and

winter (2005) periods in the Caldecott tunnel, Berkeley, California. We also obtained size-resolved emission factors for semi-volatile and particle-phase PAHs down to 10 nm Dp. PAH, CO and CO₂ samples were collected in Bore 1 (mix of ILDV and HDD) and Bore 2 (LDV only) of the Caldecott tunnel. Our results (in preparation for publication) showed that total PAH levels (i.e. vapor + particle phase concentration, in ng/m³) were similar in both bores during summer and winter periods, with NAP accounting for 90% of the total PAH mass during both seasons. In general, for PAHs with molecular weight (MW) >178 slightly higher concentrations were found during the winter period at both bores, while higher levels of naphthalene, acenaphthene, and fluorene were observed in summer. The most significant difference between Bore 2 and Bore 1 was observed for two of the higher molecular weight PAHs (benzo[g,h,i]perylene, and indeno[1,2,3-cd]pyrene; their concentrations were two times higher in the LDV-only bore. Using these results, we calculated emission factors (emfs), separately, for LDV and HDD. LDV emfs for total PAHs (vapor + particle phase) are 2 times higher in winter (2005) compared with summer (2004); HDD emfs are three times higher in winter. Emfs for PAHs with molecular weights between 178 and 252 are ca. 4 times higher for HDD while PAHs with MW>252 are practically all emitted by LDVs. Comparing PAH emfs in PM_{2.5} obtained in summer 2004 with those obtained in summer 1997 (8 years latter), a higher reduction was observed for HDD as compared with LDV; average reduction emission factors of 6 and 17 were obtained for total PAHs from LDV and HDD, respectively. These results are being written up for submission to publication in the journal *Environmental Science & Technology*.

Conclusions

A major conclusion of this study is that PAHs found in the Aitken size range represent a previously unreported particle size range, adding a fourth mode to the typical PAH size distributions found in ambient air in the nucleation, accumulation and coarse size modes. In terms of health significance, this finding is important because of the increased deposition efficiency in the alveolar area of the human respiratory tract of particles in the 10–32 nm diameter range. Particles in this size range may enter cellular and subcellular walls of target eukaryotes (Li, et al., 2000, 2004).

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